

(19)



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European Patent Office
Office européen des brevets



(11)

EP 0 675 162 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
13.01.1999 Bulletin 1999/02

(51) Int Cl.⁶: **C08L 9/00, C08L 51/04,
B60C 1/00, B60C 17/00**

(21) Application number: **95104186.2**

(22) Date of filing: **22.03.1995**

(54) **High modulus low hysteresis rubber compound for pneumatic tires**

Kautschukmischung für Reifen mit hohem Elastizitätsmodul und geringer Hysterese

Composition de caoutchouc pour pneumatique à module d'élasticité élevé et à basse hystérésis

(84) Designated Contracting States:
DE ES FR GB IT

(30) Priority: **31.03.1994 US 220765**

(43) Date of publication of application:
04.10.1995 Bulletin 1995/40

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(56) References cited:
EP-A- 0 551 829 **EP-A- 0 604 833**
EP-A- 0 606 597

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Description**TECHNICAL FIELD**

5 This invention relates to novel sulfur-vulcanizable rubber compounds having high modulus and low hysteresis. Such compounds can be utilized in various components of pneumatic tires and particularly in pneumatic safety tires which have a wall stiffness such that when the tire is punctured during running, it can bear the load of the vehicle to allow for continued high speeds for a relatively long distance until the proper repair or tire replacement can be made. More particularly, compounds of the present invention can be employed in components of safety tires having a high
10 profile with a section height of at least 12.7 cm (5 inches). One such tire component is a sidewall insert. While the compounds of the present invention may comprise ingredients that are currently commercially available, the particular combination and proportions in which they are used was not previously known.

BACKGROUND OF THE INVENTION

15 Various tire constructions have been devised over the years which enable a tire to run in an underinflated or non-inflated condition, such as after receiving a puncture and loss of air, for extended periods of time and at relatively high speeds, to enable the vehicle operator to safely drive the vehicle to an appropriate location for repair or replacement of the punctured tire. Certain of these safety tires, referred to as "run flat tires", have been successful for certain
20 applications and embody various types of tire constructions. Many such run flat tires achieve their run flat property by the placement of reinforcing layers or members of relatively stiff elastomeric material in the sidewall areas of the tire where they enable the tire to support the vehicle weight even with the complete loss of internal air pressure.

Examples of various prior art run flat tire constructions are set forth in the following patents:

25 U.S. Pat. No. 3,911,987 discloses a low profile motorcycle tire which has an elastomeric internal reinforcement that enables the tire to stay inflated for a short duration with little or no air pressure. This reinforcing layer has a Shore A hardness of at least 45, preferably within the range of 60 to 90, and is positioned either outwardly of two tire body carcass plies or between the two carcass plies. This elastic reinforcement is constructed with varying thicknesses, and is cross-sectioned to eliminate abrupt changes of effective hardness of the sidewall and reinforcing layer.

30 U.S. Pat. No. 3,949,798 discloses another run flat tire construction for a low profile tire having reinforcing rubber insert strips located between the inner strips located between the inner liner and body ply carcass of the tire sidewall.

U.S. Pat. No. 3,954,131 discloses a safety tire which has elastomeric internal reinforcements in the sidewalls which permit the tire to be used for short durations with little or no air pressure within the tire. The elastomeric side reinforcements are of varying thicknesses and are positioned outwardly of the tire carcass.

35 U.S. Pat. No. 4,067,372 discloses a pneumatic radial tire having internal reinforcements in its sidewalls which are formed of hard rubber and are used in combination with the body carcass plies and tire bead rubber inserts to give additional stiffness to the supple portions of the tire. The body carcass plies are located outwardly of the rubber inserts and are made from several cord fabric radial plies, and extend completely to the bead area of the tire.

40 U.S. Pat. No. 4,202,393 discloses a low profile motorcycle tire that has sidewall reinforcements to allow for a run flat condition in which the reinforcements are composed of an elastic filler with a reinforcing ply positioned completely around the elastic filler.

U.S. Pat. No. 4,203,481 discloses a run flat tire construction having reinforcing inserts made from a high modulus, low hysteresis rubber compound, which are located inwardly of the reinforcing carcass plies of the tire.

45 U.S. Pat. No. 4,261,405 shows another run flat tire construction for a low profile tire having a specially constructed rubber insert mounted between the inner liner and body ply carcass in the sidewall of the tire, in order to achieve the required rigidity for supporting the vehicle in an uninflated condition.

50 U.S. Pat. No. 4,287,924 discloses another run flat safety tire with sidewall reinforcing members. These members are comprised of two components, one of which is more flexible than the other, having a hardness rating greater than 70 and the other having a hardness rating of between 80 and 95. These reinforcing members are encased in the carcass plies of the tire and have a heat conducting layer positioned between the two components of the supporting members to alleviate heating problems in the thickest portions of the supporting members.

U.S. Pat. No. 4,365,659 discloses a run flat safety tire which has sidewall reinforcements made from low heat build up rubber which are positioned between an inner protective layer and the outer carcass plies of the tire.

55 U.S. Pat. No. 4,917,164 discloses the use of crescent-shaped reinforcing layers in the sidewalls of the tire to allow the tire to run for short durations with little or no air pressure. The reinforcing layers are of varying thickness and have a Shore A hardness of between 65 and 85, and are positioned between the innerliner and carcass plies of the tire. The wall thickness of the reinforcing members is between 1 and 12 millimeters.

Although many of these run flat tire constructions set forth in the above-referenced patents, have proven to be successful for certain applications, all these constructions pertain to low profile tires, that is a tire having a section

height less than 12.7 cm (5 inches) and are of the type usually found on high performance vehicles (such as racing cars) or motorcycles, and rely almost entirely on the stiffness of the elastomeric insert to provide the support for the uninflated tire. Furthermore, these high performance and motorcycle tires carry relatively smaller loads when compared to the higher weights carried by the larger cars using the higher section height tires.

Heretofore, providing a run flat tire with a high profile tire construction, that is, a run flat tire having a section height of 12.7 cm (5 inches) or greater, has not proved successful due to the relatively large sidewall reinforcement members which would be required to adequately support the tire in an uninflated condition to enable the tire to run for a relatively long distance at a high rate of speed. The relatively large rubber inserts required would increase the weight of the tire to an unacceptable limit and would materially detract from its ride characteristic. If the amount of or type of material in these relatively large sidewall inserts were reduced or changed in order to lessen the weight of the tire and improve its ride characteristics, excessive heat would be generated within the inserts during a run flat operation, resulting in the rapid destruction of the tire, thus preventing the desired run flat conditions from being achieved at usual highway speeds for satisfactory use on such tires on most passenger vehicles.

Patents have also addressed the addition of metal salts of organic acids to rubbers compositions. U.S. Pat. No. 4,076,255, for instance discloses a golf ball having a central core comprising a cis-polybutadiene elastomer, and a monomer capable of grafting-with the elastomer and comprising a metal salt of an unsaturated carboxylic acid and a polyol ester or anhydride of a polybasic unsaturated carboxylic acid.

U.S. Pat. No. 4,824,899 discloses rubber compositions suitable for use in a bead filler of a tire which composition contains a metal salt of an acrylic acid with no mention of the latter being grafted to the rubber which is either natural or a blend with a synthetic diene rubber.

U.S. Pat. No. 4,929,684 discloses a sidewall for pneumatic tires comprising natural rubber, addition polymerized synthetic rubber and blends thereof, with zinc dimethacrylate. No mention of grafting is provided as the metal salt is only employed as a reinforcing filler to increase the static tensile modulus of the rubber stock. Alternative additives for this purpose disclosed by the patent include chopped cellulose and styrene acrylonitrile resin.

Nevertheless, a sulfur-vulcanizable rubber compound having sufficiently high modulus for use in tire components or structural elements so as to allow the resulting tire to have run flat characteristics is not described in the foregoing art. The need has existed for a rubber compound for use in components such as sidewall inserts for high profile pneumatic safety or run flat tires. This need has not been met by known rubber compounds.

SUMMARY OF THE INVENTION

Thus, it is an object of the present invention to provide a sulfur-vulcanizable, peroxide-free rubber compound that possesses high modulus, low hysteresis and Shore A hardness within a specific high range subsequent to vulcanization.

It is another object to provide a sulfur-vulcanizable, peroxide-free rubber compound as above that can be employed to manufacture components or structural elements of pneumatic tires which exhibit run flat characteristics.

It is yet another object of the present invention to provide a sulfur-vulcanizable, peroxide-free rubber compound as above that can be employed to manufacture components of pneumatic tires having a section height of 5 inches or greater.

It is still another object of the present invention to provide a sulfur-vulcanizable, peroxide-free rubber compound that is useful to manufacture structural components of pneumatic tires including sidewall inserts, bead filler structures, high speed insert structures and the like.

It is yet another object of the present invention to provide a sulfur-vulcanizable, peroxide-free rubber compound having properties of high modulus, low hysteresis and sufficient stiffness to be useful in the construction of pneumatic tires and provide the necessary reinforcing effect required to enable the tire to support the vehicle in a run flat condition.

At least one or more of the foregoing objects, together with the advantages thereof over known rubber compounds and the use thereof in pneumatic tires which shall become apparent from the specification which follows, are accomplished by the invention as hereinafter described and claimed.

In general, the present invention pertains to a sulfur-vulcanizable rubber compound, being devoid of peroxide components and capable of being worked prior to vulcanization, having high modulus and low hysteresis properties subsequent to vulcanization comprising:

100 parts by weight of an uncured grafted rubber copolymer containing from 25 to 55 parts by weight of polyisoprene;

from 75 to 45 parts by weight of a diene polymer selected from the group consisting of homopolymers of conjugated diene monomers and copolymers thereof with monoolefin monomers and EPDM terpolymers, to total 100 parts by weight of rubber polymer,

wherein a portion of at least one of said polyisoprene and said diene polymers is grafted with a polymeric metal

salt of an α,β -ethylenically unsaturated carboxylic acid to form said uncured graft rubber copolymer; from 50 to 70 parts by weight of a reinforcing filler, per 100 parts by weight of said grafted rubber copolymer, and at least 4 parts by weight of a curative selected from the group consisting of sulfur and sulfur donors, per 100 parts by weight of said grafted rubber copolymer; and
 5 wherein the sulfur-vulcanizable rubber compound, upon vulcanization, has a $\tan \delta$ of from 0.03 to 0.20, measured at 100°C, 7% deflection and 10 Hz, and blow-out time measured according to ASTM Test Procedure D-623 of greater than 3 hours.

The present invention also provides a sulfur-vulcanizable rubber compound, being devoid of peroxide components, and capable of being worked prior to vulcanization, having high modulus and low hysteresis proper-ties subsequent to vulcanization comprising:

100 parts by weight of an uncured grafted rubber copolymer containing
 from 25 to 55 parts by weight of polyisoprene;
 15 from 75 to 45 parts by weight of a diene polymer selected from the group consisting of homopolymers of conjugated diene mono-mers and copolymers thereof with monoolefin monomers and EPDM terpolymers, to total 100 parts by weight of rubber polymer;
 wherein a portion of at least one of said polyisoprene and said diene polymer is grafted with a polymeric metal salt of an α,β -ethylenically unsaturated carboxylic acid by a process using an effective amount of azo-bis-isobutyronitrile as a free radical initiator to form an uncured graft rubber copolymer;
 20 from 50 to 70 parts by weight of a reinforcing filler, per 100 parts by weight of said grafted rubber copolymer, and at least 4 parts by weight of a curative selected from the group consisting of sulfur and sulfur donors, per 100 parts by weight of said grafted rubber copolymer; and
 wherein the sulfur-vulcanizable rubber compound, upon vulcanization, has a $\tan \delta$ of from 0.03 to 0.20, measured
 25 at 100°C, 7% deflection and 10 Hz, and a blow-out time measured according to ASTM Test Procedure D-623 of greater than 3 hours.

The present invention also provides a component or structural element for a pneumatic tire comprising the aforementioned sulfur-vulcanizable rubber compounds.

30 Finally, the present invention provides a pneumatic tire having run flat properties imparted to it by at least one of the aforementioned structural components.

BRIEF DESCRIPTION OF THE DRAWING

35 The drawing figure provides a cross-sectional view of a high profile tire whose construction is designed for run flat operation according to the invention.

PREFERRED MODE FOR CARRYING OUT THE INVENTION

40 As noted hereinabove the present invention is directed toward sulfur-vulcanizable rubber compounds, being devoid of peroxide components, having high modulus, low hysteresis and a specific hardness range subsequent to vulcanization which are useful in the manufacture of high aspect ratio pneumatic tires, particularly safety tires possessing run flat characteristics. Physical properties that are necessary for the structural components of a run flat tire and that are possessed by the compounds of the present invention include stiffness, low heat build up and good resistance to heat.
 45 Stiffness, which is determined by high modulus and high hardness, is necessary to minimize sidewall displacement in run flat, or underinflated, conditions. Low heat build up is attributed to low hysteresis properties resulting in compounds which are cooler running and impart increased tire life under run flat operating conditions. Finally, good heat resistance is also necessary to increase the life of the tire operating under run flat conditions. For good heat resistance it is necessary that the compound possess good aging and reversion resistance properties.

50 Rubber compounds, according to the present invention, comprise natural or synthetic polyisoprene, with natural polyisoprene being preferred, and elastomeric diene polymers including polybutadiene and copolymers of conjugated diene monomers with at least one monoolefin monomer. The rubber compounds provide the required low hysteresis and low heat build up properties, the polybutadiene rubber providing low hysteresis and low compression set, and the polyisoprene providing low hysteresis and high tensile strength. Suitable polybutadiene rubber is elastomeric and has a 1,2-vinyl content of 1 to 3 percent and a cis-1,4 content of 96 to 98 percent. Other high vinyl butadiene rubbers,
 55 having up to about 12 percent 1,2-content, may also be suitable with appropriate adjustments in the level of other components, and thus, substantially any high vinyl, elastomeric polybutadiene can be employed. The copolymers may be derived from conjugated dienes such as 1,3-butadiene, 2-methyl-1,3-butadiene-(isoprene), 2,3-dimethyl-1,2-buta-

diene, 1,3-pentadiene, 1,3-hexadiene and the like, as well as mixtures of the foregoing dienes. The preferred conjugated dienes is 1,3-butadiene. Regarding the monoolefinic monomers, there include vinyl aromatic monomers such as styrene, alpha-methyl styrene, vinyl naphthalene, vinyl pyridine and the like as well as mixtures of the foregoing monoolefins. The copolymers may contain up to 50 percent by weight of the monoolefin based upon total weight of copolymer. The preferred copolymer is a copolymer of a conjugated diene, especially butadiene, and a vinyl aromatic hydrocarbon, especially styrene. Preferably the diene polymer content of the rubber compound can comprise up to 25 percent by weight of styrene-butadiene random copolymer, preferably 7 to 10 percent by weight.

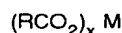
The above-described copolymers of conjugated dienes and their method of preparation are well known in the rubber and polymer arts. Many of the polymers and copolymers are commercially available. It is to be understood that practice of the present invention is not to be limited to any particular rubber included hereinabove or excluded.

An EPDM terpolymer rubber can also be utilized to form the backbone portion of the graft copolymer of the invention. The term "EPDM" is used in the sense of its definition as found in ASTM-D-1418-64 and is intended to mean a terpolymer of ethylene, propylene and a diene monomer. Illustrative methods for preparing such terpolymers are found in U.S. Pat. No. 3,280,082 and British Pat. No. 1,030,289. The preferred terpolymers contain from 40 to 80 weight percent ethylene and from 1 to 10 weight percent of the diene with the balance of the terpolymer being propylene.

The diene monomer utilized in forming the EPDM terpolymer is preferably a non-conjugated diene. Illustrative examples of non-conjugated dienes which may be employed are dicyclopentadiene, alkyldicyclopentadiene, 1,4-pentadiene, 1,4-hexadiene, 1,5-hexadiene, 1,4-heptadiene, 2-methyl-1,5-hexadiene, cyclooctadiene, 1,4-octadiene, 1,7-octadiene, 5-ethylidene-2-norbornene, 5-n-propylidene-2-norbornene, 5-(2-methyl-2-butenyl)-2-norbornene and the like. A typical EPDM is Viatalon 2504 (Exxon Chemical Co.), a terpolymer having a Mooney Viscosity (ML, 1 + 8, 100°C) of about 40 and having 50 weight percent of ethylene, 45 weight percent of propylene and 5.0 weight percent of 5-ethylidene-2-norbornene with an \bar{M}_n as measured by GPC of about 47,000 and an \bar{M}_w as measured by GPC of about 174,000.

A preferred EPDM is Royalene® 521 (Uniroyal Chemical Co.), a terpolymer having a Mooney Viscosity (ML/4/100°C) of about 50 and having 50 weight percent of ethylene, 43 weight percent of propylene and 6.6 weight percent of ethylidene norbornene.

The high modulus and high hardness properties can be attained by using monomers derived from certain polymerizable metal salts of α , β -ethylenically unsaturated carboxylic acids. These monomers have the formula



where R is an α , β -ethylenically unsaturated acyclic moiety having 2 to 7 carbon atoms such as acrylic, methacrylic, cinnamic and crotonic acids of which acrylic and methacrylic acids are preferred; M is a metal ion selected from the group consisting of sodium, potassium, magnesium, calcium, zinc, barium, aluminum, tin, zirconium, lithium and cadmium of which zinc and magnesium are preferred; and x is an integer corresponding to the valence of M. A particularly preferred monomer for this use is zinc dimethacrylate, which may alternatively be referred to as a metal salt.

In the present invention, zinc dimethacrylate or other metal salt of an α , β -ethylenically unsaturated carboxylic acid, is combined with at least one of the rubber polymers disclosed hereinabove in a grafting reaction such that the polymer of the metal salt is grafted onto the polymeric backbone. More specifically, poly zinc dimethacrylate is preferably grafted to the rubber polymers by a free radical graft copolymerization, as discussed hereinbelow. Unlike the existing state of the art which has provided for the addition of such metal salts to the rubber compound as a filler or pigment, the present invention calls for the preparation of a polymer derived from the metal salt of an α , β -ethylenically unsaturated carboxylic acid, which is grafted from at least one of the rubber polymers.

The graft copolymer can be prepared by a relatively uncomplicated procedure. Thus, the graft copolymer can be prepared by first dissolving an unsaturated hydrocarbon rubber of the type described above such as polybutadiene in a solvent such as hexane, then adding the monomeric metal salt of an unsaturated carboxylic acid such as zinc dimethacrylate to the polymer solution, adding a free radical initiator such as azo-bis-isobutyronitrile to the polymer solution and then heating the reaction mixture at a temperature of from 40° to 150°C for a time period of from 0.1 to 100 hours to form the graft copolymer which, by the nature of the preparation is freely processable and uncured.

Hydrocarbon solvents which may be employed in the preparation of the graft copolymers include aromatic and aliphatic hydrocarbons in which the rubber polymers are soluble. Suitable hydrocarbon solvents include hexane, heptane, pentane, octane, cyclohexane, cycloheptane, cyclopentane, methyl cyclohexane, benzene and toluene. The preferred hydrocarbon solvents are hexane and toluene.

The monomeric metal salt (e.g., zinc dimethacrylate) is preferably added to the resultant rubber polymer solution contained in a suitable reactor in the form of a fine powder with stirring and under a nitrogen atmosphere to form a dispersion of the metal salt in the rubber polymer solution. While not essential, it is often desirable and preferred to add a surfactant along with the metal salt to the polymer solution in order to provide for a more stable dispersion of

the metal salt in the polymer solution. The preferred surfactants for that purpose are nonionic octylphenoxy polyethoxy ethanol surfactants available from Rohm and Haas Company under the designations Triton X-15, Triton X-45 and Triton X-100.

As indicated, a free radical initiator is then added to the rubber polymer solution containing the metal salt to effect graft polymerization of the metal salt to the polymer backbone. It is generally preferred to seal the reactor containing the polymer solution and dispersed metal salt prior to adding the initiator and then to add the initiator in liquid form under pressure to the reactor. Suitable free radical initiators which may be added to the rubber polymer solution for that purpose include di-sec-butyl peroxydicarbonate; t-amyl peroxy pivalate; 2,5-dimethyl-2,5-di-(2-ethylhexanoyl-peroxy) hexane; t-amyl peroxy-2-ethylhexanoate; t-butyl-2-ethylhexanoate; 2,2-azo-bis-(2-methylpropionitrile) and other hydrocarbon solutions.

After addition of the free radical initiator is completed, the reaction mixture is heated at a temperature of from 40 to 150°C for a time period of from 0.1 to 100 hours to produce the graft copolymer.

The graft copolymers can be recovered from the reaction medium by various conventional methods such as alcohol coagulation, steam desolventization, thermal desolventization and the like. Additionally, solvent may be removed from the graft copolymer by drum drying, extruder drying, vacuum drying and the like.

It is not possible to practice the present invention by adding to the rubber polymer(s) zinc metal, or other metal, and an α,β -ethylenically unsaturated carboxylic acid. Instead, the metal salt of the acid must be added to a solution of the rubber as previously described, forming a poly zinc dimethacrylate or other polymeric graft with the rubber polymer. Moreover, the resulting graft copolymer rubber must be uncured which is important to the utility of the rubber. In the manufacture of a tire or other vulcanizable rubber article, for instance, the graft rubber forming the particular tire component must remain uncured in order to allow mixing of the other components and also to ensure good and complete adhesion to the surrounding components which are vulcanized together to form the tire or other rubber article.

Zinc dimethacrylate, when added to certain rubber compounds as a pigment, has been known to impart high modulus and high hardness properties. However, when the metal salt is added to the rubber polymers in the grafting reaction, superior properties such as flex fatigue are also imparted to the rubber compound as compared to those compounds wherein the zinc dimethacrylate has merely been added as a pigment. Improved compressive flex fatigue is determined according to ASTM Testing Procedure D-623. As described in U.S. Pat. No. 4,465,829, a blow-out time ranging from 95 to 150 minutes is measured by this ASTM Test and relates to flex fatigue. For purposes of the present invention, a blow-out time exceeding 180 minutes (3 hours) is deemed to be satisfactory for use as a component of a run-flat tire.

The rubber compounds of the present invention comprise from 25 to 55 parts by weight of polyisoprene, and from about 45 to 75 parts by weight of a diene polymer selected from the group consisting of homopolymers of conjugated diene monomers and copolymers thereof with monoolefin monomers and EPDM terpolymers, to total 100 parts by weight of rubber (phr). A portion of at least one of these rubber polymers is present as the grafted polymer. In other words, the total rubber compound includes a portion of polyisoprene and polybutadiene or diene copolymer which is not grafted and a portion which has become part of the grafted polymer. The grafted portion may be taken from either rubber polymer portion or from a portion of both.

The grafted rubber copolymer, according to the present invention is uncured and comprises 60 to 80 weight percent base (that is, substrate) polymer and 40 to 20 weight percent of the zinc dimethacrylate polymer or polymer of another monomer derived from a related metal and/or a related α,β -ethylenically unsaturated carboxylic acid.

Additionally, the compounds of the present invention comprise from about 50 to 70 phr of carbon black as a low hysteresis filler material. Particularly useful is FEF (fast extrusion furnace) black, a relatively high structure and large particle size carbon black namely, 40 mm, 40 m²/g, particle size and surface area, respectively. Further discussions of such carbon blacks can be found in the literature. See, for example, The Vanderbilt Rubber Handbook, pp 408-424, RT Vanderbilt Co., Norwalk, CT 06855 (1979) and Rubber Technology, 2d ed., pp 51-59, Van Nostrand Reinhold Corporation (1973).

The inventive compounds are cured by sulfur, rather than peroxides and thus, a sulfur curing agent, such as sulfur or a sulfur donor is required. Minimally, at least about 4 phr of sulfur, or an equivalent amount of donor, is added to the compound to provide high modulus. In the present invention, addition of a sulfur in oil blend is generally preferred, with the mixture comprising about 80 percent by weight of sulfur and 20 percent by weight of oil. The oils employed are conventional rubber processing oils. Conventional cure accelerators are also employed to provide fast modulus generation during cure. The inventive compounds also include from about 1 to 3 phr of an antioxidant and an antiozonant of conventional types, (employed in the usual amounts) to impart good heat resistance to the compound.

As will be appreciated by those skilled in the art, because the compounds are cured by sulfur, they do not contain any peroxide curatives or other peroxide components. If one of the latter were present in the rubber formulation, the higher temperatures encountered during mixing and compounding would likely be sufficient to cure the rubbers, rendering a mass unsuitable for the manufacture of the desired rubber component which is ultimately subjected to a separate heat-initiated vulcanization to activate the sulfur or other sulfur donor present in the formulation.

Regarding physical properties of the rubber compounds of the present invention, a normalized, mechanical static

modulus of from 9.6 to 27.6 MPa (1400 psi to 4000 psi) is suitable, the preferred range being between 17.9 and 19.3 MPa (2600 psi and 2800 psi), with approximately 18.6 MPa (2700 psi) being most preferred. These moduli are at the run flat operating condition (0 psi inflation) and are measured at 15% strain. The hardness range should be within from 72 and 97 on the Shore A hardness scale, at 23°C, the preferred range being between 72 and 90, with 88 being most preferred. Likewise, the hysteresis when measured at 100°C at 10 Hertz and 7 percent deflection, has a tan Delta (6) of from 0.03 to 0.20, with the preferred range falling between 0.03 and 0.11 and most preferably, between 0.03 and 0.08.

As an example of a high modulus, low hysteresis, hard sulfur-vulcanizable, peroxide-free rubber compound according to the present invention a rubber blend formulation has been provided in Table I, as Compound 1. The zinc dimethacrylate grafted polybutadiene is designated as Zn(Ma)₂PBd in Table I. All non-rubber parts are presented on the basis of parts by weight per hundred rubber by weight (phr). To the right of Compound 1, Table I lists a range of suitable amounts for each component. Notably, the ranges listed for polyisoprene and polybutadiene includes the polyisoprene and polybutadiene rubber employed by itself and as part of the grafted polymer. Thus, no range is shown for the zinc methacrylate polymer per se.

The compounds of the present invention can contain conventional antioxidants, antiozonants and accelerators, as is shown for Compound 1. It is to be understood that such components are well known to those skilled in the art and thus, the present invention is not limited to the use of any particular antioxidants, antiozonants or accelerators, or amounts thereof. Similarly, practice of the present invention is also not limited to the specific formulation of Compound 1.

TABLE I
HIGH MODULUS, LOW HYSTERESIS,
HARD SULFUR-VULCANIZABLE, PEROXIDE-FREE RUBBER COMPOUNDS

	<u>COMPOUND 1</u>	<u>RANGES</u>
5		
10	Natural rubber	25.0
	Zn(Ma) ₂ PBd	52.0*
15	Polybutadiene (ungrafted)	40.0
	FEF carbon black	57.0
20	Zinc oxide	5.7
	Stearic acid	1.14
25	Naphthenic oil	0.56
	Antioxidant ^a	2.27
30	Antiozonant ^b	1.14
	Sulfur/oil (80/20)	8.52
35	Accelerator ^c	1.70
	Accelerator ^d	0.56
40	Accelerator ^e	0.56

* contains 35 phr polybutadiene and 17 phr zinc methacrylate

a) 1,2-dihydro-2,2,4-trimethylquinoline (TMQ)

b) N-octyl, N'-phenyl-p-phenylene diamine

c) 2-(morpholinothio)benzothiazolesulfenamide (MBS)

d) tetramethylthiuram monosulfide (TMTM)

e) benzothiazyl disulfide (MBTS)

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Compound 1 was subjected to cure at 170°C for 15 minutes following which physical properties were measured and are reported in Table II.

TABLE II

PHYSICAL PROPERTIES OF COMPOUND 1	
Modulus (unaged)	
tensile (psi) MPa	(2330) 16.1
% elongation (at break)	167
Modulus (aged) 2 days @ 100°C	
tensile (psi) MPa	(2130) 14.7
% elongation (at break)	122
Modulus (low extension) (psi) (non normalized)	
5%	(93.0) 0.6 MPa
10%	(172.0) 1.2 MPa
20%	(289.0) 2.0 MPa
Durometer Shore A	
23° C	81
66° C	79
MTS tan δ	
(23°C, 10Hz, 7% def)	0.135
(66°C, 10Hz, 7% def)	0.091
(100°C, 10Hz, 7% def)	0.074
(150°C, 10Hz, 7% def)	0.069
Pendulum rebound	
23°C	56
100°C	72
Dynamic modulus	
150°C 10Hz	(2350 psi) 16.2 MPa

From the results reported in Table II, it is apparent that the rubber compound of the present invention provided high modulus, low hysteresis and a relatively high Shore A hardness.

As further examples of high modulus, low hysteresis, hard sulfur-vulcanizable, peroxide-free rubber compounds according to the present invention, additional rubber blend formulations have been provided in Table III, as Compounds 2-7. The zinc dimethacrylate polymer was grafted onto the polybutadiene (Compounds 2-5 and 7); the polyisoprene (Compound 3); the EPDM (Compound 5); and the SBR (Compound 7). Additionally, a Control Compound is presented which contained zinc dimethacrylate (ZDMA) but only as a filler, not as a polymer grafted to any of the rubber. All non-rubber parts are presented on the basis of parts by weight per hundred rubber by weight (phr). Unlike Table I, Table III also lists the actual parts of rubber in each recipe.

The compounds of the present invention can contain conventional antioxidants, antiozonants and accelerators, as are presented in Table III. Again, it is to be understood that such components are well known to those skilled in the art and thus, the present invention is not limited to the use of any particular antioxidants, antiozonants or accelerators, or amounts thereof. Accordingly, practice of the present invention is also not limited to the specific formulations of Compounds 2-7.

TABLE III

HIGH MODULUS, LOW HYSTERESIS,

HARD SULFUR-VULCANIZABLE, PEROXIDE-FREE RUBBER COMPOUNDS

Compounds	Control	2	3	4	5	6	7
Natural Rubber	25	25	25	25	25	25	25
Polybutadiene	75	40	25	30	--	40	40
EPDM	--	--	--	--	25	--	--
PBD-g-33% ZDMA	--	35	25	45	25	--	35
PI-g-20% ZDMA	--	--	25	--	--	--	--
EPDM-g-33% ZDMA	--	--	--	--	25	--	--
SBR(10/90)-G-33% ZDMA	--	--	--	--	--	35	--
actual parts of rubber in the recipe	100	88	87	95	87	88	88
FEF C/B	50	50	50	50	50	50	50
ZDMA	18	--	--	--	--	--	--
ZnO	5	5	5	5	5	5	5
Stearic Acid	1	1	1	1	1	1	1
Zn stearate	--	--	3	3	3	--	--
Resin ^a	--	--	--	--	1	--	--
Naphthenic Oil	0.5	0.5	0.5	0.5	--	0.5	0.5
Antioxidant ^b	1	1	1	1	1	1	1
Antioxidant ^c	2	2	2	2	1	2	2

TABLE III(Continued)

Sulfur/Oil (4/1)	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5
Accelerator ^d	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Accelerator ^e	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Accelerator ^f	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
a) resorcinol formaldehyde resin								
b) 1,2-dihydro-2,2,4-trimethylquinoline (TMQ)								
c) N-octyl, N'-phenyl-p-phenylene diamine								
d) 2-(morpholinothio)benzothiazolesulfenamide (MBS)								
e) tetramethylthiuram monosulfide (TMTM)								
f) benzothiazyl disulfide (MBTS)								

Compounds 2-7 and the Control were subjected to cure at 170°C for 15 minutes following which physical properties were measured and are reported in Table IV.

TABLE IV
PHYSICAL PROPERTIES OF COMPOUNDS 2-7

Cured @ 170°C for 15 minutes	Control	2	3	4	5	6	7
Tensile (psi) MPa	(1615) 11.1	(2330) 16.1	(1890) 13.0	(1790) 12.3	(1870) 12.9	(1860) 12.8	(1590) 11.0
Tensile aged 2 d @ 100°C, (psi) MPa	(1756) 12.1	(2130) 14.7	(1480) 10.2	(1350) 9.3	--	--	--
Elong, %	117	167	111	98	108	140	204
Elong aged 2d @ 100°C, %	102	122	69	60	--	--	--
5% Mod, (psi) MPa	(132) 0.91	(93) 0.64	(113) 0.78	(116) 0.86	--	(120) 0.83	(82) 0.57
10% Mod, (psi) MPa	(230) 1.59	(172) 1.19	(197) 1.36	(205) 1.41	(385) 2.65	(212) 1.46	(135) 0.93
20% Mod, (psi)	(389) 2.68	(289) 1.99	(340) 2.34	(355) 2.44	(586) 4.64	(364) 2.51	(218) 1.50
Shore A @ 23°C	85	81	84	85	88	80	76
Shore A @ 100°C	83	79	83	84	81	79	73
Tan Delta, 10 Hz, 7% def. @							
23°C	0.109	0.135	0.094	0.097	0.091	--	--
66°C	0.085	0.091	0.053	0.063	--	--	--
100°C	0.081	0.074	0.041	0.051	--	--	--
150°C	0.079	0.069	--	--	0.105	--	--
Rebound @ 23°C	61	56	61	60	50	70	61
Rebound @ 100°C	72	72	77	70	53	79	74
Dynamic Mod @ 150°C, (psi) MPa	(2700) 18.6	(2350) 16.2	--	--	--	--	--

TABLE IV (Continued)

Firestone Flex Blow Out @ 55 lbs^a

Time to Blow Out	64 min	3 hrs NF	3 hrs NF	3 hrs NF
Temp @ End of test, °C	>245°	202°	179°	185°
Block Cond.	disintegrated	solid	solid	solid
Tire Testing							
Run Flat(Miles) Kilometres				56 (35)	..	113 (70)	
Rolling Loss,(Lbs.) kg				5.02 (11.07)	..	(11.37)	5.16

a) ASTM Testing Procedure D-623

The section designated Tire Testing in Table IV was conducted utilizing Compounds 5-7. Experimental tires constructed with Compounds 5 and 7 were successful in run-flat condition to the extent reported in Table IV. Experimental tires constructed with Compound 6 were built in which the aspect ratio was varied from 60 to 55 to 50 in a solid tread

tire, *i.e.*, not tread pattern. This construction provided very low mileage, as expected, although the run flat miles increased by 30 and 64 percent in going to aspect ratios of 55 and 50, respectively, from the base aspect ratio of 60. Actual mileage and rolling loss was not reported and was not conducted for the other rubber Compounds.

As noted hereinabove, the rubber compounds of the present invention can be employed to manufacture components of pneumatic tires. With reference to the drawing figure, a tire cross-section has been presented, depicting typical components of a high profile pneumatic tire. The tire referred to generally by the numeral 1, includes a tread portion 2 terminating in a pair of tread shoulders 3 adjacent a pair of sidewalls 4, which extend radially from the axial outer shoulders 3 to a pair of bead portions indicated generally at 6. As in a typical pneumatic tire, the interior of the tire includes an innerliner 7 formed of a high air impervious material, in combination with a pair of body plies 8 and 9 which form the carcass of the tire. Body plies 8 and 9 extend around bead portion 6 and terminate in turn-up ends 10 and 11 respectively. Each bead portion 6 consists of a usual annular bead wire 13 and a bead filler of generally triangular-shaped cross-section 14. Abrasive gum strips 16 preferably are molded with the finished tire and are adapted to be located adjacent each flange of a wheel rim on which the tire is to be mounted.

Usual reinforcing belts of wire and/or fabric 12 are located between body carcass plies 8 and 9 and tread portion 2. These tire components are all contained within integrally formed inner and outer rubber casings which form the sidewalls of the tire. The tire section height is indicated at "H", and in accordance with the objects of the present invention, a height of at least 12.7 cm (5 inches) or greater is contemplated; such tires are referred to herein as high profile tires. In passenger tire nomenclature, such as P 225/60 R 16, the number 225 represents the section width of the tire in millimeters; 16 represents the tire diameter in inches, and 60 represents the ratio in percentage of the tire section height with respect to the section width, *i.e.*, the aspect ratio. Thus far, the above-referenced tire construction is illustrative of a general pneumatic tire construction which can vary.

Additionally the tire depicted in the drawing includes several new components which assist in providing a high profile, pneumatic safety tire. One of these is the sidewall insert which comprises a pair of generally crescent-shaped elastomeric reinforcing members indicated at 21 which are mounted between innerliner 7 and body plies 8 and 9 and extend from adjacent tread shoulders 3 of tread portion 2 along the sidewall of the tire to a position generally adjacent the apex 22 of bead filler 14. Another component comprises a pair of biased reinforcing strips or plies 25, which are located between sidewalls 4 and body carcass plies 8 and 9, and elastomeric reinforcing members 21, the latter extending along the sidewall of the tire to a position below apex 22 of bead filler 14. For a more detailed description of such a tire construction, particularly designed for run flat operation as a safety tire, see co-pending application, U.S. Ser. No. 07/680,714.

The sulfur-vulcanizable, peroxide-free rubber compounds of the present invention have particular applicability to the formation of the sidewall inserts 21. Additionally, they can be employed in the formation of the bead filler 14. Of course, use of the compounds of the present invention is not limited solely to the manufacture of components for pneumatic tires, but these can be utilized wherever a sulfur-vulcanizable rubber compound having high modulus, low hysteresis and relatively high Shore A hardness properties subsequent to vulcanization is desired, as will be apparent to those skilled in the art.

In conclusion, it should be clear from the foregoing example and specification disclosure that the compounds of the present invention have improved physical properties which can, in turn, improve the run flat performance of pneumatic tires when they are used to make components incorporated therein. It is to be understood that practice of the present invention is not limited to the natural rubber formulation of Compound 1 exemplified herein or by the disclosure of typical rubber polymers provided herein, and that the example has been provided merely to demonstrate practice of the subject invention. Those skilled in the art may readily select and formulate other high modulus, low hysteresis sulfur-vulcanizable rubber compounds according to the disclosure made hereinabove.

Moreover, as noted hereinabove, the present invention should not be limited to the use of such rubber compounds as sidewall inserts for pneumatic tires or even to components of pneumatic tires *per se*.

Claims

1. A sulfur-vulcanizable rubber compound, being devoid of peroxide components and capable of being worked prior to vulcanization, having high modulus and low hysteresis proper-ties subsequent to vulcanization comprising:

100 parts by weight of an uncured grafted rubber copolymer containing

from 25 to 55 parts by weight of polyisoprene;

from 75 to 45 parts by weight of a diene polymer selected from the group consisting of homopolymers of conjugated diene mono-mers and copolymers thereof with monoolefin monomers and EPDM terpolymers, to

total 100 parts by weight of rubber polymer;

wherein a portion of at least one of said polyisoprene and said diene polymers is grafted with a polymeric metal salt of an α,β -ethylenically unsaturated carboxylic acid to form said uncured graft rubber copolymer;

from 50 to 70 parts by weight of a reinforcing filler, per 100 parts by weight of said grafted rubber copolymer, and

at least 4 parts by weight of a curative selected from the group consisting of sulfur and sulfur donors, per 100 parts by weight of said grafted rubber copolymer; and

wherein the sulfur-vulcanizable rubber compound, upon vulcanization, has a $\tan \delta$ of from 0.03 to 0.20, measured at 100°C, 7% deflection and 10 Hz, and a blow-out time measured according to ASTM Test Procedure D-623 of greater than 3 hours.

2. A sulfur-vulcanizable, peroxide-free rubber compound, as set forth in claim 1, wherein the mechanical static modulus of said vulcanized rubber compound ranges from 9.6 to 27.6 MPa (1400-2000 psi) at 15% strain.

3. A sulfur-vulcanizable, peroxide-free rubber compound, as set forth in claim 1, having a Shore A hardness of from 72 to 97 subsequent to vulcanization.

4. A sulfur-vulcanizable, peroxide-free rubber compound, as set forth in claim 1, wherein said uncured grafted rubber copolymer comprises:

from 60 to 80 percent by weight of at least one of said polyisoprene and said diene polymer, and

from 20 to 40 percent by weight of said polymeric metal salt of said α,β -ethylenically unsaturated carboxylic acid.

5. A sulfur-vulcanizable, peroxide-free rubber compound, as set forth in claim 4, wherein said polymeric metal salt of said α,β -ethylenically unsaturated carboxylic acid is poly zinc dimethacrylate.

6. A sulfur-vulcanizable, peroxide-free rubber compound, as set forth in claim 1, wherein said reinforcing filler comprises carbon black.

7. A sulfur-vulcanizable rubber compound, being devoid of peroxide components, and capable of being worked prior to vulcanization, having high modulus and low hysteresis proper-ties subsequent to vulcanization comprising:

100 parts by weight of an uncured grafted rubber copolymer containing

from 25 to 55 parts by weight of polyisoprene;

from 75 to 45 parts by weight of a diene polymer selected from the group consisting of homopolymers of conjugated diene mono-mers and copolymers thereof with monoolefin monomers and EPDM terpolymers, to total 100 parts by weight of rubber polymer;

wherein a portion of at least one of said polyisoprene and said diene polymer is grafted with a polymeric metal salt of an α,β -ethylenically unsaturated carboxylic acid by a process using an effective amount of azo-bis-isobutyronitrile as a free radical initiator to form an uncured graft rubber copolymer;

from 50 to 70 parts by weight of a reinforcing filler, per 100 parts by weight of said grafted rubber copolymer, and

at least 4 parts by weight of a curative selected from the group consisting of sulfur and sulfur donors, per 100 parts by weight of said grafted rubber copolymer; and

wherein the sulfur-vulcanizable rubber compound, upon vulcanization, has a $\tan \delta$ of from 0.03 to 0.20, measured at 100°C, 7% deflection and 10 Hz, and a blow-out time measured according to ASTM Test Procedure D-623 of greater than 3 hours.

8. A structural component for a pneumatic tire comprising the sulfur-vulcanizable rubber compound claimed in claims 1 to 7.
- 5 9. A structural component for a pneumatic tire, as set forth in claim 8, comprising a sidewall insert having a crescent-shaped cross-section.
10. A structural component for a pneumatic tire, as set forth in claim 8, comprising a bead filler.
- 10 11. A pneumatic tire having run flat properties imparted by at least one structural component claimed in claims 8 to 10.

Patentansprüche

- 15 1. Schwefel-vulkanisierbare Kautschukmasse ohne Peroxidkomponenten, die dazu imstande ist, vor der Vulkanisation bearbeitet zu werden und die einen hohen Modul und niedere Hystereseeigenschaften nach der Vulkanisation aufweist, enthaltend:

100 Gew.-Teile eines nichtvulkanisierten gepfropften Kautschukcopolymeren, das
20 25 bis 55 Gew.-Teile Polyisopren,

75 bis 45 Gew.-Teile eines Dienpolymeren, ausgewählt aus der Gruppe bestehend aus Homopolymeren von konjugierten Dienmonomeren und Copolymeren davon mit Monoolefinmonomeren und EPDM-Terpolymeren, auf jeweils 100 Gew.-Teile Kautschukpolymeres,
25 wobei ein Teil von mindestens einem des Polyisoprens und der genannten Dienpolymeren mit einem polymeren Metallsalz einer α,β -ethylenisch ungesättigten Carbonsäure gepfropft ist, um das genannte nichtvulkanisierte Pfropf-Kautschuk-Copolymere zu bilden,
30 50 bis 70 Gew.-Teile eines Verstärkungsfüllstoffs je 100 Gew.-Teile des gepfropften Kautschukcopolymeren und

mindestens 4 Gew.-Teile eines Vulkanisationsmittels, ausgewählt aus der Gruppe bestehend aus Schwefel und Schwefeldonatoren, pro 100 Gew.-Teile des genannten gepfropften Kautschukcopolymeren und
35 wobei die Schwefel-vulkanisierbare Kautschukmasse nach der Vulkanisation einen $\tan\delta$ -Wert von 0,03 bis 0,20, gemessen bei 100°C, 7% Ablenkung und 10 Hz und eine Blow-out-Zeit, gemessen nach der ASTM-Testverfahrensweise D-623, von größer als 3 Stunden hat.
- 40 2. Schwefel-vulkanisierbare, Peroxid-freie Kautschukmasse nach Anspruch 1, dadurch **gekennzeichnet**, daß der mechanische statische Modul der vulkanisierten Kautschukmasse im Bereich von 9,6 bis 27,6 MPa (1400-2000 psi) bei 15% Spannung liegt.
- 45 3. Schwefel-vulkanisierbare, Peroxid-freie Kautschukmasse nach Anspruch 1, dadurch **gekennzeichnet**, daß sie eine Shore-A-Härte von 72 bis 97 nach der Vulkanisation hat.
4. Schwefel-vulkanisierbare, Peroxid-freie Kautschukmasse nach Anspruch 1, dadurch **gekennzeichnet**, daß das nichtvulkanisierte gepfropfte Kautschukcopolymere folgendes enthält:
50 60 bis 80 Gew.-% von mindestens einem von dem genannten Polyisopren und dem genannten Dienpolymeren, und

20 bis 40 Gew.-% des polymeren Metallsalzes der α,β -ethylenisch ungesättigten Carbonsäure.
- 55 5. Schwefel-vulkanisierbare, Peroxid-freie Kautschukmasse nach Anspruch 4, dadurch **gekennzeichnet**, daß das polymere Metallsalz der α,β -ethylenisch ungesättigten Carbonsäure Polyzinkdimethacrylat ist.
6. Schwefel-vulkanisierbare, Peroxid-freie Kautschukmasse nach Anspruch 1, dadurch **gekennzeichnet**, daß der

Verstärkungsfüllstoff Ruß umfaßt.

7. Schwefel-vulkanisierbare Kautschukmasse ohne Peroxidkomponenten, die dazu imstande ist, vor der Vulkanisation bearbeitet zu werden und die einen hohen Modul und niedrige Hystereseeigenschaften nach der Vulkanisation aufweist, enthaltend:
 - 100 Gew.-Teile eines nichtvulkanisierten gepfropften Kautschukcopolymeren, das 25 bis 55 Gew.-Teile Polyisopren,
 - 75 bis 45 Gew.-Teile eines Dienpolymeren, ausgewählt aus der Gruppe bestehend aus Homopolymeren von konjugierten Dienmonomeren und Copolymeren davon mit Monoolefinmonomeren und EPDM-Terpolymeren, auf jeweils 100 Gew.-Teile Kautschukpolymeres,
 - wobei ein Teil von mindestens einem des Polyisoprens und der genannten Dienpolymeren mit einem polymeren Metallsalz einer α,β -ethylenisch ungesättigten Carbonsäure durch ein Verfahren, bei dem eine wirksame Menge von Azobisisobutyronitril als freier Radikalinitiator verwendet wird, gepfropft worden ist, um ein nicht-vulkanisiertes gepfropftes Kautschukcopolymeres zu bilden,
 - 50 bis 70 Gew.-Teile eines Verstärkungsfüllstoffs je 100 Gew.-Teile des gepfropften Kautschukcopolymeren und
 - mindestens 4 Gew.-Teile eines Vulkanisationsmittels, ausgewählt aus der Gruppe bestehend aus Schwefel und Schwefeldonatoren, pro 100 Gew.-Teile des genannten gepfropften Kautschukcopolymeren, und
 - wobei die Schwefel-vulkanisierbare Kautschukmasse nach der Vulkanisation einen $\tan\delta$ -Wert von 0,03 bis 0,20, gemessen bei 100°C, 7% Ablenkung und 10 Hz und eine Blow-out-Zeit, gemessen nach der ASTM-Testverfahrensweise D-623, von größer als 3 Stunden hat.
8. Strukturkomponente für einen pneumatischen Reifen, umfassend die Schwefel-vulkanisierbare Kautschukmasse nach den Ansprüchen 1 bis 7.
9. Strukturkomponente für einen pneumatischen Reifen nach Anspruch 8, dadurch **gekennzeichnet**, daß sie einen Seitenwandeinsatz mit einem Halbmondförmigen Querschnitt umfaßt.
10. Strukturkomponente für einen pneumatischen Reifen nach Anspruch 8, dadurch **gekennzeichnet**, daß sie einen Wulstfüller umfaßt.
11. Pneumatischer Reifen mit flachen Laufeigenschaften, die durch mindestens eine Strukturkomponente nach den Ansprüchen 8 bis 10 verliehen worden sind.

Revendications

1. Composition de caoutchouc vulcanisable au soufre, exempte de composants du type peroxyde et apte à être travaillée avant vulcanisation, ayant des propriétés de haut module et de faible hystérésis après vulcanisation, comprenant :
 - 100 parties en poids d'un copolymère caoutchouc greffé non vulcanisé contenant 25 à 55 parties en poids de polyisoprène ;
 - 75 à 45 parties en poids d'un polymère diénique choisi dans le groupe consistant en homopolymères de monomères diéniques conjugués et en copolymères de ces monomères avec des monomères mooléfiniques et en terpolymères EPDM, pour un total de 100 parties en poids de polymère caoutchouc ;
 - où une fraction de l'un au moins du polyisoprène et des polymères diéniques est greffée avec un sel métallique polymère d'un acide carboxylique à non-saturation α,β -éthylénique pour former le copolymère caoutchouc greffé non vulcanisé ;
 - 50 à 70 parties en poids d'une charge de renforcement, pour 100 parties en poids du copolymère caoutchouc greffé, et
 - au moins 4 parties en poids d'un agent vulcanisant choisi dans le groupe consistant en le soufre et des don-

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neurs de soufre, pour 100 parties en poids du copolymère caoutchouc greffé ; et où la composition de caoutchouc vulcanisable au soufre, après vulcanisation, a une valeur $\tan \delta$ de 0,03 à 0,20, mesurée à 100°C, 7 % de fléchissement et 10 Hz, et un temps de rupture par éclatement, mesuré conformément à la méthode d'essai ASTM D-623, supérieur à 3 heures.

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2. Composition de caoutchouc exempte de peroxyde, vulcanisable au soufre selon la revendication 1, pour laquelle le module mécanique statique de la composition de caoutchouc vulcanisée se situe dans la plage de 9,6 à 27,6 MPa (1400-2000 lb/in²) pour une déformation de 15 %.

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3. Composition de caoutchouc exempte de peroxyde, vulcanisable au soufre suivant la revendication 1, ayant une dureté Shore A de 72 à 97 après vulcanisation.

4. Composition de caoutchouc exempte de peroxyde, vulcanisable au soufre, suivant la revendication 1, dans laquelle le copolymère caoutchouc greffé non vulcanisé comprend :

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60 à 80 % en poids de l'un au moins du polyisoprène et du polymère diénique indiqués, et 20 à 40 % en poids du sel métallique polymère de l'acide carboxylique à non-saturation α,β -éthylénique en question.

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5. Composition de caoutchouc exempte de peroxyde, vulcanisable au soufre, suivant la revendication 4, dans laquelle le sel métallique polymère de l'acide carboxylique à non-saturation α,β -éthylénique est un diméthacrylate de zinc polymère.

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6. Composition de caoutchouc exempte de peroxyde, vulcanisable au soufre, suivant la revendication 1, dans laquelle la charge de renforcement comprend du noir de carbone.

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7. Composition de caoutchouc vulcanisable au soufre, exempte de composants du type peroxyde et apte à être travaillée avant la vulcanisation, ayant des propriétés de haut module et de faible hystérésis après vulcanisation, comprenant :

100 parties en poids d'un copolymère caoutchouc greffé non vulcanisé contenant

25 à 55 parties en poids de polyisoprène ;

75 à 45 parties en poids d'un polymère diénique choisi dans le groupe consistant en homopolymères de monomères diéniques conjugués et en copolymères de ces monomères avec des monomères mono-oléfiniques et en terpolymères EPDM, pour un total de 100 parties en poids du polymère caoutchouc ;

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où une fraction de l'un au moins du polyisoprène et du polymère diénique est greffée avec un sel métallique polymère d'un acide carboxylique à non-saturation α,β -éthylénique par un procédé utilisant une quantité efficace d'azo-bis-isobutyronitrile comme initiateur de radicaux libres pour former un copolymère caoutchouc greffé non vulcanisé ;

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50 à 70 parties en poids d'une charge de renforcement, pour 100 parties en poids du copolymère caoutchouc greffé, et

au moins 4 parties en poids d'un agent vulcanisant choisi dans le groupe consistant en soufre et donneurs de soufre,

pour 100 parties en poids du copolymère caoutchouc greffé ; et

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la composition de caoutchouc vulcanisable au soufre, après vulcanisation, a une valeur $\tan \delta$ de 0,03 à 0,20, mesurée à 100°C, 7 % de fléchissement et 10 Hz, et un temps de rupture par éclatement, mesuré conformément à la méthode d'essai ASTM D-623, supérieur à 3 heures.

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8. Composant de structure pour un bandage pneumatique, comprenant la composition de caoutchouc vulcanisable au soufre suivant les revendications 1 à 7.

9. Composant de structure pour bandage pneumatique suivant la revendication 8, comprenant une pièce insérée dans les flancs ayant une section transversale en forme de croissant.

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10. Composant de structure pour bandage pneumatique suivant la revendication 8, comprenant une bandelette support de talon.

11. Bandage pneumatique ayant des propriétés de roulement à plat conférées par au moins un composant de structure

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suivant les revendications 8 à 10.

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